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Lithium and the Foreseeable Future

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LITHIUM AND THE FORESEEABLE FUTURE

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Bachelor of Science in Mechanical Engineering

By

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Contents

Abstract

This paper aims to clarify the uncertainties regarding worldwide lithium resource availability in the years to come. Previous studies made on the subject are presented with some ambiguity and this work intends to fill the gaps. The information and data presented throughout this script with respect to global lithium resources and reserves are mostly based on data released by the United States Geological Survey (USGS). Lithium resource availability in the future is a point of paramount significance primarily for the automotive, portable electronics, and the power generation industry. Since, a change of supply would ultimately affect the price of lithium, which would then affect the industries mentioned. Theoretical scenarios and predictions about future lithium supply and demand are presented at the latter part of this paper intended to give the reader a better understanding of the actual size of the total global lithium resources.

1. Introduction

With the effects of climate change in these recent years, mankind is forced to seek alternative ways to generate electricity and to commute. Since most vehicles today are internal combustion engine vehicles, the air contamination caused by the combustion of fossil fuels is very high. Transportation and electricity generation is responsible for approximately 56% of all the greenhouse gas emissions in the planet [1]. Opting for hybrid and electric vehicles would reduce the contamination of the atmosphere. Most fossil fuel deposits, such as oil and natural gas won't last more than 50 years at the current rate of consumption, so change is inevitable anyways [2]. Some promising alternative clean and renewable ways of generating electricity are solar energy and wind power. Both methods mentioned require a module to store the energy it generates, in most cases a battery is used. Most batteries used for this application are made of lithium-ion technology. If solar energy and wind power is used to generate electricity in the future as the two primary sources of energy, a lot of batteries would be required to store energy.

The increase in popularity of electric and hybrid vehicles will continue to increase over the years and the demand for lithium-ion batteries will increase accordingly. It is evident that the automotive industry is changing by transitioning from internal combustion vehicles to hybrid and electric vehicles. With the increase in demand for electric and hybrid vehicles, a lot of lithium will be required to supply the batteries with lithium-ion technology. The questions regarding changes in the lithium market that remain to be answered are: how much lithium can be found in resource deposits around the world? And how long will those resources last with the predicted increase in demand of clean transportation and electricity generation? Other than batteries for solar/wind power plants and electric vehicles there are other applications where lithium is used that leave uncertainties with regards to the reserves of lithium.

1.1 Background

The objective of this research paper is to identify current lithium reserves and resources to get a grasp on how much lithium is available and if it is enough to supply the increasing demand of lithium for the next decades. The term reserve, refers to deposits that are known to exist with a reasonable amount of certainty based on studies. And resource is the total amount of material that exists, that is, the discovered and undiscovered material as well as the economically recoverable and the not recoverable [3]. It is essential to know how much lithium exists in the world today. Future developments in the lithium-ion battery technology sector depend upon the availability of the material in the future, because if there is not enough lithium, other material alternatives could be explored. To this day, it is not clear how large lithium resources are around the world. Therefore, we cannot estimate future predictions on how long we can rely on lithium-ion technology.

In this paper, the distribution of lithium reserves around the world will be explored. The process of extracting lithium from minerals and salt-brines will be analyzed to give a better understanding of where lithium comes from and how the lithium-ion industry works in the present day. It is important to understand current procedures for extracting lithium, since the process for extracting lithium from one source differs from another depending on the properties and location of the source.

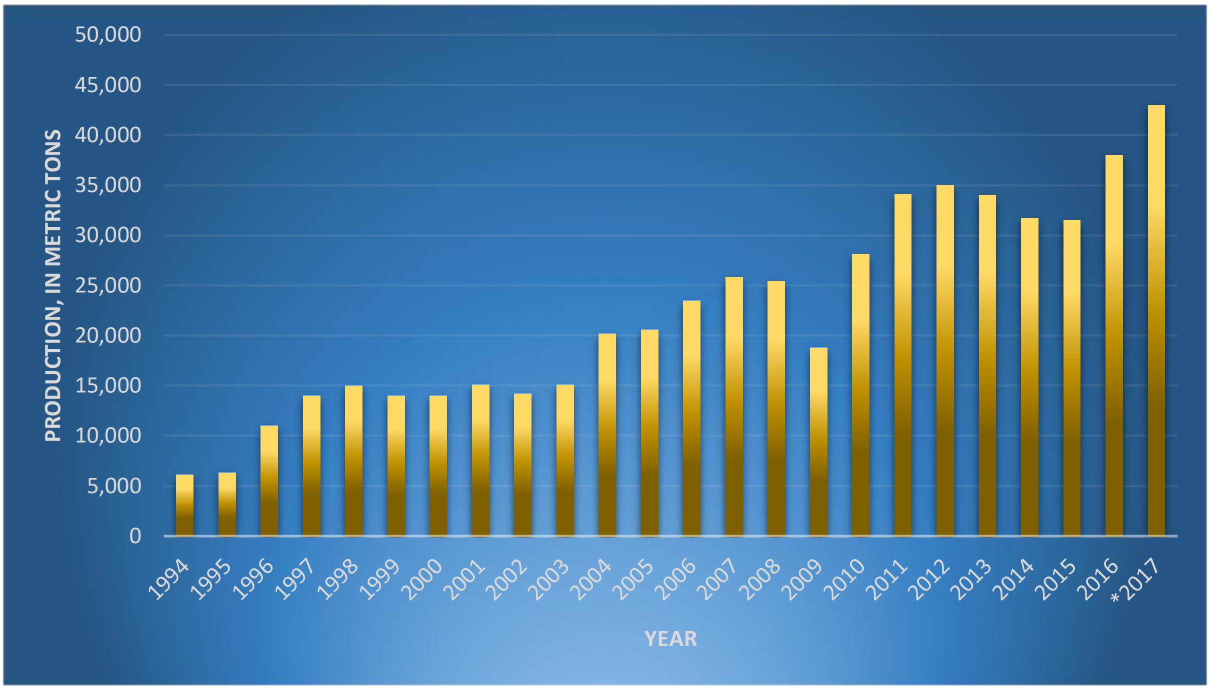

Figure 1.1. Graph showing lithium mine production worldwide (excluding United States.) Values are in metric tons. Own work using data from U.S. Geological Survey (2018). *Estimated. [26].

Lithium is usually extracted by two methods: extraction from salt-brines and from spodumene (mineral). Both methods of extraction will be explained briefly. In figure 1.1, the worldwide production of lithium from salt-brines and spodumene, combined, is shown. Australia is the largest producer of lithium currently, with 14.1 thousand tons of lithium produced in 2015 [25]. Australia extracts lithium mainly from spodumene and most if not all of what is produced is exported to China. The second largest producer of lithium is Chile followed by Argentina and China subsequently.

By inspection of the data that is presented later in the paper, today's main lithium supplier, Australia, does not have sufficient lithium resources to stay as the largest lithium supplier in the world for far too long. Countries in South America will more than likely take over Australia's market. Bolivia is just in the beginning stages of producing lithium carbonate and is expecting to produce 15,000 tons of lithium carbonate by the end of 2018

[27]. Lithium carbonate typically is composed of 18.8% lithium, therefore, Bolivia would be producing about 2,820 tons of lithium by the end of 2018.

2. Lithium Distribution, Reserves and Resources

The largest lithium deposits worldwide, are situated in South America. The salt-flats located in Argentina, Bolivia, and Chile hold more than 50% of all the lithium resources in the world. China and the United states also have a significant amount of lithium. The United States lithium resources are mostly in the form of spodumene so the extraction of lithium is not economically feasible compared to lithium extraction from salt-brines. Lithium production in the US is currently very low due to the process required to extract lithium from spodumene, a lot of energy is required to process the raw material.

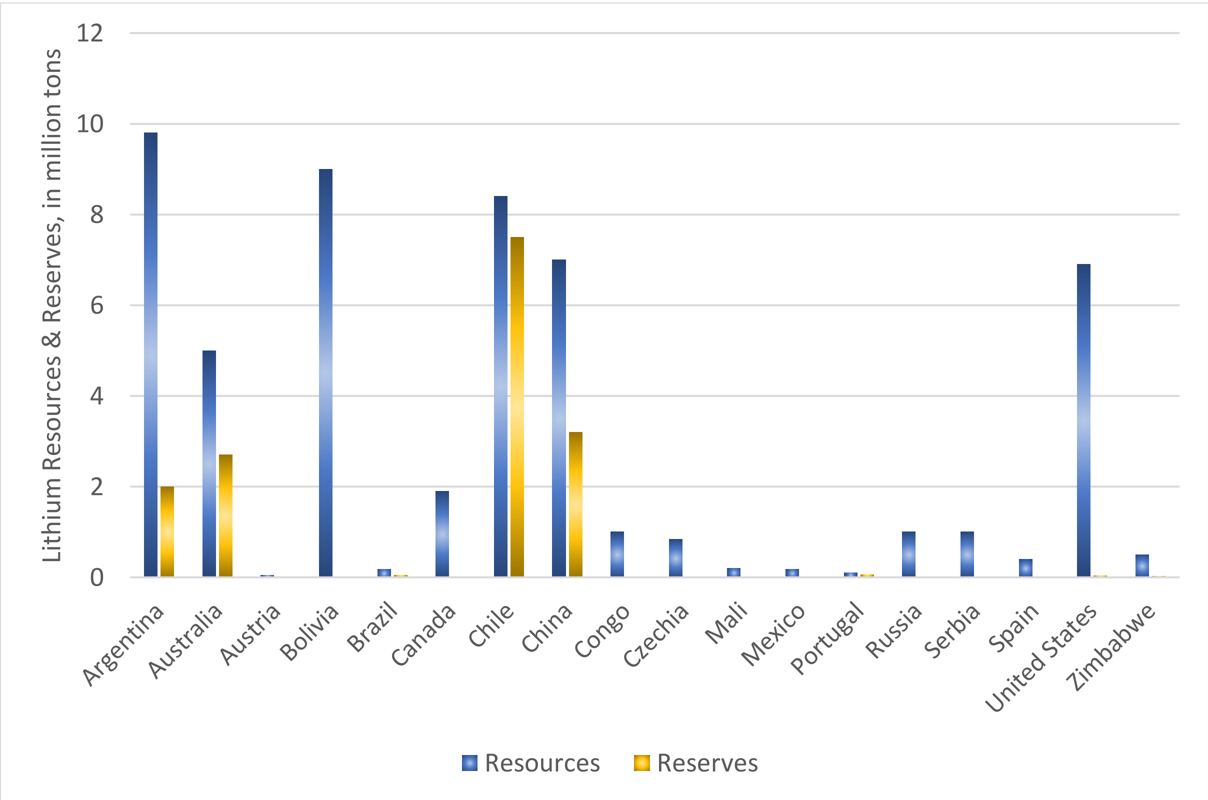

Figure 2.1. Graph showing lithium resources and reserves worldwide. Values are in metric tons. Data are from U.S. Geological Survey (2017). [4 – 26].

Lithium resources and reserves are shown in figure 2.1. As explained previously, reserves are deposits that are known to exist with reasonable amount of certainty based on studies. And resources are the total amount of material, which include the discovered deposits, the undiscovered deposits, the economically recoverable and the nonrecoverable. The data presented is the information on lithium resources and reserves that is currently known. However, there may be more resources of lithium in the world that has not been discovered yet. Recently, there has been a lot of discussion about lithium resources located in Afghanistan. There are claims that Afghanistan is the "Saudi Arabia of lithium" [28]. Nevertheless, there is no confirmed information of the size of the lithium resources in Afghanistan to this day.

Chile has the largest lithium reserve in the planet, with 7.5 million metric tons. Argentina and Bolivia are known to have the largest lithium resources with 9.8 million metric tons and 9 million metric tons respectively. Nevertheless, the country with the largest lithium production in 2015 was Australia. Australia is one of the biggest exporters of lithium in the world and they extract lithium from minerals with high concentration of lithium, which make the process of extraction economically feasible despite the high costs of the method employed [29].

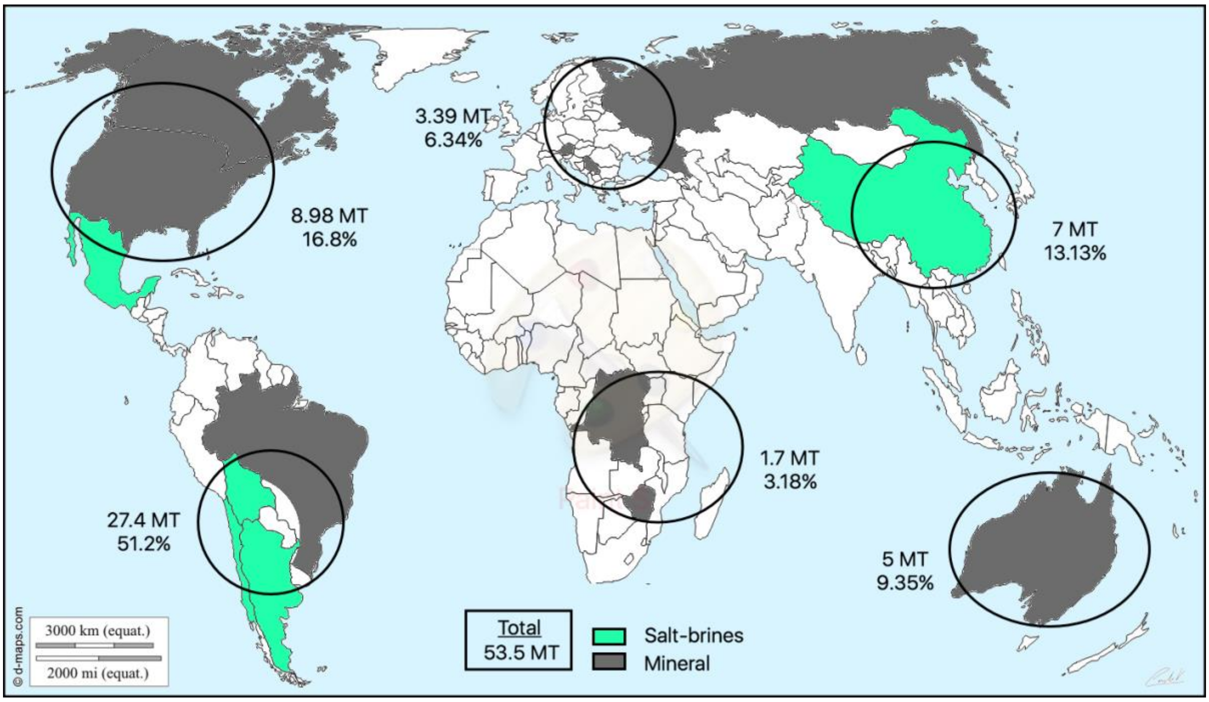

Figure 2.2. Map showing the locations of lithium resources in million tons. Based on data from USGS [4 – 26, 30]. Base map from d-maps.com [31].

In figure 2.2, the distribution of total worldwide lithium resources is shown. Lithium resources from mineral and salt brine deposits combined, is conveyed. I would like to point out that the information portrayed is not entirely accurate, since the current methods to calculate mineral resources are not precise. The data will vary between institutions who made the studies and calculations about resources and reserves. In this case the data presented is from the United States Geological Survey, so the values may vary from other studies.

3. Process of Lithium Extraction and Cost

Lithium is typically extracted from the mineral spodumene and from brine-lake, salt-pan deposits or salt flats. The extraction process of lithium from brine-lakes, salt-pan deposits, and salt flats is very similar, and it is the most feasible choice of the two, spodumene being the alternative. The energy requirements for the extraction and treatment of lithium from salt flats is low compared to the process involving spodumene, therefore the cost to process the lithium from salt flats is lower. Nevertheless, spodumene deposits with high concentrations of lithium can compensate for the high costs involved with the processing of spodumene.

Australia and Chile are mass producers of lithium and they supply almost all the lithium used in hybrid, electrical vehicles and portable electronics in the world. Australia processes its lithium from spodumene rich in lithium. And Chile extracts its lithium from salt flats [32].

3.1 Extraction from Salt Flats

The extraction process of lithium from salt flats involve several transitions between ponds. First the brine material is pumped from underground brine wells into a pond where it is expected to evaporate allowing it to concentrate. Then the concentrated brine is pumped to another pond where sodium chloride is expected to crystalize and precipitate. The brine is moved to more ponds where more sodium chloride precipitation occurs, after moving the brine into several ponds, slaked lime is added to the calcium and magnesium salt precipitates forming gypsum and magnesia. The precipitants may vary depending on the composition of the salt brine. In this specific scenario the brine is comprised of Mg, Ca, and Na compounds. The process of adding slaked lime is repeated until Mg, Ca, and Na salts is depleted, leaving a brine consisting of 0.5% lithium. The brine is transported to the process plant where lithium carbonate (Li_2CO_3) is extracted. An energy evaluation shows that the energy needed to process lithium carbonate is 40.2 MJ/kg [32]. In figure 3.1.1, the process of lithium extraction from salt brines is shown.

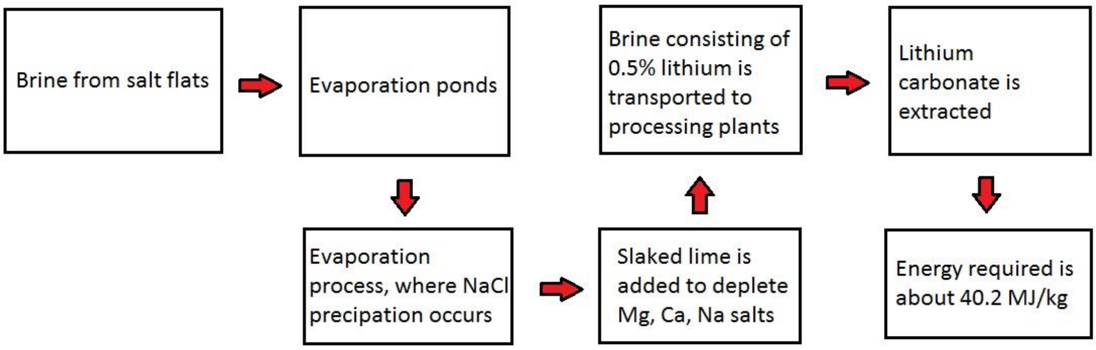

Figure 3.1.1. Lithium extraction from salt brines [32, 33].

3.2 Extraction from Spodumene

Another way to extract lithium is via spodumene. Spodumene is a mineral consisting of lithium aluminum inosilicate ($LiAl(SiO_3)_2$). After extracting the mineral, it must be heat treated at 1000 degrees Celsius to change its microscopic structure from an alpha to a beta to enhance acid leaching, typically this is done using sulfuric acid. Because of this process lithium salts are recovered. This process to extract lithium is significantly higher in cost than the salt flats extraction, due to the heat treatment that the ore must go through. This practice has been abandoned in the United States, since lower cost processes was introduced. However, the United States is planning to reconsider the production of lithium from minerals to enhance U.S production [32]. In figure 3.2.1, the process of extracting lithium from minerals is shown.

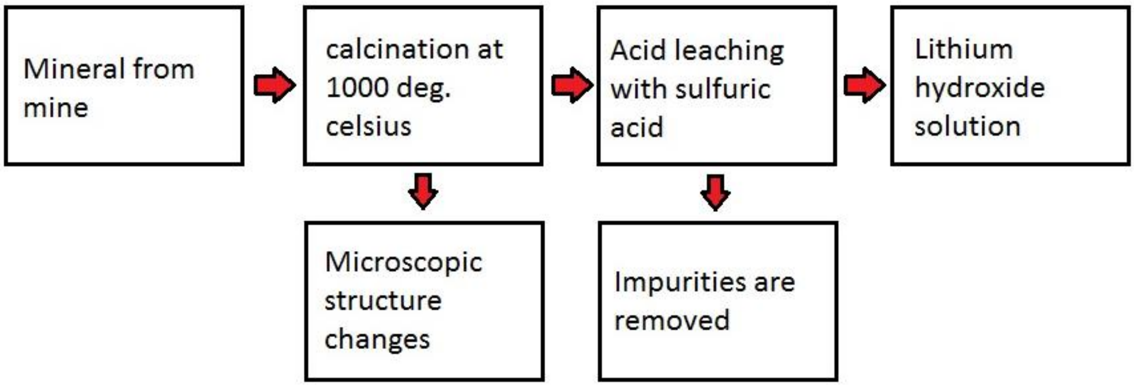

Figure 3.2.1 Lithium extraction from Spodumene [32, 34].

3.3 Lithium Price

With global warming around the corner and the current rate of consumption of fossil fuels, demand for lithium and other battery materials will indisputably increase. Some countries like Bolivia are on the initial stages of producing lithium carbonate. Nevertheless, the price of lithium will continue to rise. Some studies show that as the prices of fossil fuels increased, the demand for electric and hybrid vehicles increased.

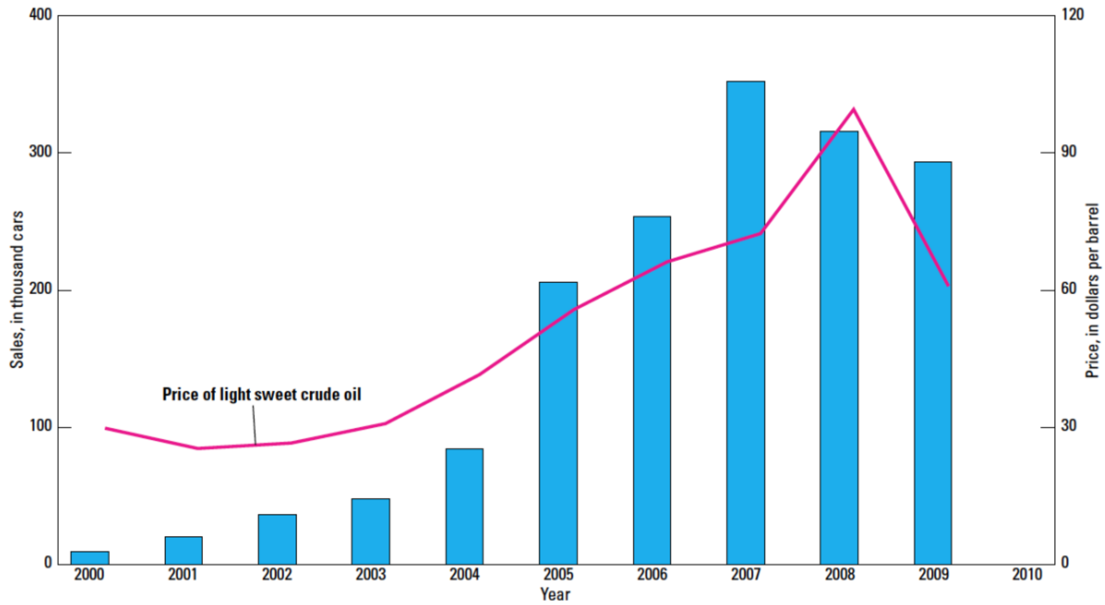

Figure 3.3.1 Graph showing sales of hybrid vehicles in the United States and the price of light sweet crude oil [35].

In figure 3.3.1, the demand for hybrid vehicles and the price of light sweet crude oil is shown to be positively related. The graph shows that as the price of light sweet crude oil increases, the demand for hybrid electric vehicles increases. As soon as the prices of fossil fuels begin to increase drastically or as soon as some governments stop subsidizing fuel, the demand for electric and hybrid vehicles will increase. Hence, the demand for lithium and other battery materials will increase. The price increase of fossil fuels will not solely affect the automotive market. The cost of generating electricity will increase, since most countries generate electricity via fossil fuels. This, will incentivize the generation of power via renewable methods. Methods such as solar power and wind turbines, will more than likely be used, since both are clean and renewable sources of energy. These methods of generating electricity store the energy generated in an energy storage module, also known as a battery. The batteries used on energy generation plants are large. Most of these batteries are lithium-ion batteries. So, the demand of lithium will also increase as solar power and wind turbines becomes more popular.

If the demand of lithium increases, the price of lithium will be affected. The price of lithium could increase a lot if supply of lithium stays the same. Or the price could decrease if the production of lithium increases. There is no easy way to estimate this behavior since the change of lithium's demand is affected by several externalities such as, governments' decisions (i.e. subsidies). However, some studies were made that provide future price forecasts of lithium for the next couple of years.

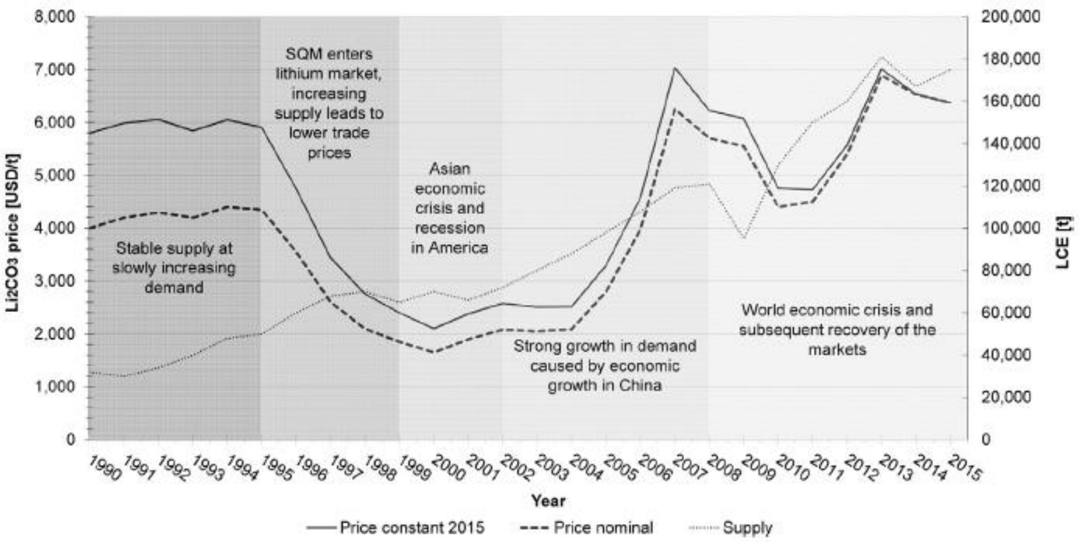

Figure 3.3.2. Lithium Price 1990-2015 [36].

In figure 3.3.2 the price of lithium carbonate and the supply of lithium carbonate equivalents (LCE) is shown from 1990 to 2015. It is important to note that the prices of lithium were stable in the early 90s, but the price of lithium carbonate soon plummeted with the market entry of SQM (Chilean chemical company) at the beginning of 1995. The increase of supply by SQM caused the price of lithium carbonate to decrease. The low prices of lithium carbonate from 1999 to 2002 were primarily due to the Asian economic crisis and the recession in North America. The increase in price that can be observed between 2004 and 2007 was mainly because of the rapid growth of the Chinese economy. Experts on the field estimate a price jump to about 25,500 USD/t by 2020 [36].

4. Current Applications

There are three main lithium-based products that dominate the lithium market. Lithium carbonate (Li_2CO_3,) which is extracted from slat brines, has the largest share in the market and it is mostly used in secondary batteries. Lithium in the form of mineral concentrates holds the second largest share in the market. It is mainly used as a raw material in the production of glass and ceramics. Lithium hydroxide is the third in the list and like lithium carbonate it is also used for secondary batteries [30]. It is important to note that lithium carbonate and lithium hydroxide are lithium-based compositions that are produced following a chemical process. Mineral concentrates are used as raw material, but it can also be processed to obtain lithium carbonate, lithium hydroxide, and other lithium-based compounds.

4.1 Lubricants

Lithium hydroxide is used as a thickening agent in greases for automotive and industrial lubrication [37].

4.2 Ceramics & Glass

Mineral concentrates and lithium carbonate are used in the ceramics and glass industry. Lithium reduces the thermal expansion coefficient of ceramic and glass, which increases the melting point of both [37].

4.3 Batteries

Due to lithium's high energy density and lack of "memory effect," lithium-based secondary batteries are currently the most efficient power source for portable electronics and electric vehicles [37]. Most of the cathodes for lithium-ion batteries that are available today in the market, are made by calcination at high temperatures. The process involves a mixture between lithium carbonate (LiCo3) and transition-metal precursors. Lithium hydroxide is also used, but the mixture is to be handled carefully. The procedure usually takes place between the temperatures of 600 and 800 degrees Celsius. The process usually requires fossil fuels to reach those temperatures.

In most lithium-ion secondary batteries the cathode is the most important element. Today, many research studies are being conducted to obtain better lithium-ion battery cathodes. Advances and improvements of lithium-ion battery cathodes could lead to higher energy density materials, lower costs of manufacturing batteries and better safety. Advances in the lithium-ion battery industry depend on advances in cathode materials.

Anodes are usually made of carbon based materials. Graphite is a very popular anode material in lithium-ion batteries. Hard carbon, soft carbon and natural graphite require a thermal process to achieve full graphitization. Coating the carbon anode materials with amorphous carbon is a procedure that protects the surface of the anode against wear under cell operation conditions.

4.4 Other

Lithium is also used in air conditioning systems, cement and adhesives, aluminum, dyes and pharmaceuticals [37].

4.5 Data

In figure 4.5.1, the demand of lithium carbonate by different applications is shown. The data shown under other, consist of applications such as: pharmaceuticals, rubber and thermoplastics. The use of lithium in secondary batteries increased drastically throughout the years. By 2009, the use of lithium in secondary batteries is the application which, demands the most lithium. The data shown is up to date and is based on estimates made by USGS. The estimates made by USGS considers the lithium extracted from brines and from minerals.

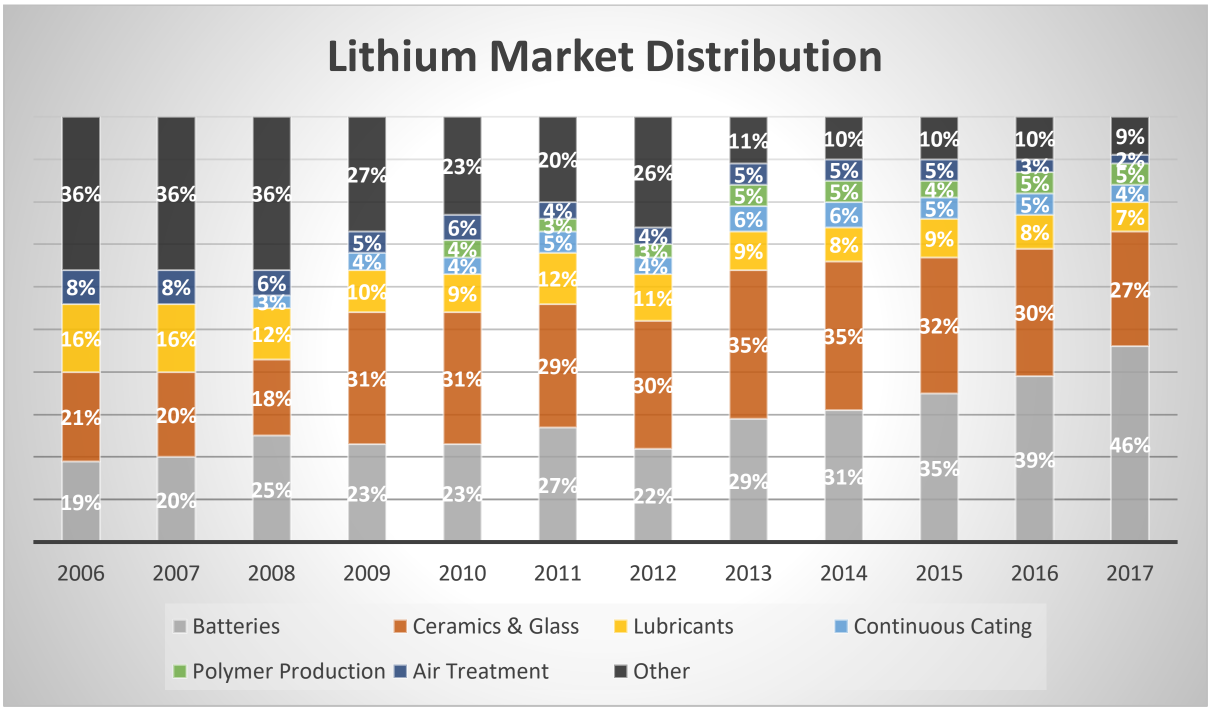

Figure 4.5.1. Lithium Market Distribution. Own work based on data from USGS. [4 – 26].

4.6 Predictions

With the data collected with respect to the size of the lithium resources, some calculations can be made to show how many batteries could be made from the global lithium resources. We can also predict how long the resources would last if we were to consume lithium at the current rate of consumption. The following calculations are based on an 85 kWh NCA battery similar to the battery used in Tesla's Model S. All the calculations are explained in detail in the appendix. According to my calculations a NCA battery with 85 kWh of energy requires 87.1 kg of raw $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) material. There is 6.29 kg of lithium in those 87.1 kg of NCA. Of all the lithium that was extracted worldwide in 2017 about 46% was destined to the manufacturing of batteries as seen in figure 4.2. To make a reasonable estimate I destined 50% of the total global lithium resources to the automotive sector. We also need to consider the fact that some deposits are not economically recoverable. We will assume that half of the world's resources are economically recoverable. Of the 53.5 million tons of lithium, 13.375 million tons will be destined only for electrical vehicles. If 6.29 kg of lithium is needed per car; out of the 13.375 million tons of lithium, 2.1 billion cars with an 85 kWh NCA battery can be built. To put that information into perspective, 79.56 million cars were sold in 2017 [38]. If we assume that the number of cars sold per year in the future will remain constant (79.56 million cars per year) and assuming that the market is restricted only to electric vehicles with an 85-kWh NCA battery; there would be enough lithium for almost 27 years. Indisputably, these assumptions are unrealistic, nevertheless, it shows that there is enough lithium to power more than 2.1 billion electric vehicles without even considering lithium recycling, other substitutes, and most importantly advances in battery technologies.

5. Conclusion & Some Remarks

Lithium is an indispensable material, today, in 2018 A.D, many applications depend upon this precious metal. Applications such as: Ceramics and glass, lubricants, pharmaceuticals, and most importantly, batteries. As this paper suggests lithium reserves and resources are not by any means scarce. With reserves of approximately 15.6 million tons and resources of about 53.5 million tons, lithium is not a limited mineral. However, there is no certainty that the abundant lithium resources explored in this paper are economically recoverable.

As Martin et al. suggests, demand for lithium will increase to an amount between 230,000 – 270,000 tons of LCE by 2020. In terms of lithium mineral that is equivalent to an increase from 43,240 – 50,760 tons of lithium. Hence, the price of LCE will suffer an increase if supply does not increase by a significant amount.

Admittedly, the recycling of lithium is an alternative to diminish future impacts of lithium availability. Lithium recovery by hydrometallurgy is a process where lithium is recovered form spent secondary lithium-ion batteries. The process involves the recovery of lithium carbonate by precipitation. Recovery of lithium from sea water is another method proposed and it can be done following two methods: co-precipitation and extraction process, and ion-exchange and sorption process [39].

Furthermore, the process of extracting lithium from sea water is less likely to become a reality. The costs involved with that process are really high since the concentration of lithium in sea water is very low, large quantities of water would have to be processed to obtain significant quantities of lithium. Regardless of the true size of the recoverable lithium resources, as Vikstrom et al. suggests, to allow a smooth transition towards electric vehicles, other types of batteries should be developed, batteries which use small amounts of lithium or other battery materials should be the focus. Since the reserves of lithium will continue to decrease, and the prices of lithium will continue to rise.

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7. Appendix

Prediction calculations:

Battery:

Cathode: NCA – $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$.

Anode: Graphite – C_6

Electrodes	Molar Mass - g/mol	Specific Capacity - mAh/g	Voltage - V
NCA (Cathode)	96.08	278.8	3.7
Graphite (Anode)	72	372	0.2

Cell energy density Calculation:

$$N = \frac{372\ mAh/g}{278.8\ mAh/g} = 1.334$$

$$Cell\ Capacity = \frac{372}{2.334} = 159.4\ mAh/g$$

$$Cell\ Voltage = 3.7\ V - 0.2\ V = 3.5\ V$$

$$Cell\ Energy\ Density = 159.4 \frac{mAh}{g} * 3.5\ V = 557.8\ Wh/kg$$

Tesla Battery:

$$85\ kWh = 85000\ Wh$$

$$Raw\ electrode\ material = \frac{85000\ Wh}{557.8\ Wh/kg} = 152.4\ kg$$

$$NCA\ composition = \frac{1.334}{2.334} * 152.4\ kg = 87.1\ kg$$

$$Lithium\ composition = \frac{6.941\ g/mol}{96.08\ g/mol} * 87.1\ kg = 6.29\ kg$$

So, the 85-kWh battery contains 6.29 kg of lithium.

The total number of electric cars with an 85-kWh NCA battery that can be manufactured with all the lithium resources assuming that only half the resources are economically recoverable and that half of that is destined for the automotive industry is:

$$Total\ Cars\ with\ 25\%\ of\ lithium\ resources = \frac{53500000000}{4} * \frac{1}{6.29} = 2{,}126{,}391{,}097\ cars$$

$$Lithium\ would\ last = \frac{2126391097\ cars}{79560000\ cars/yr} = 26.72\ yr$$